StatMech questions: Bogolubov-Born-Green-Kirkwood-Yvon hierarchy

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As usual, we consider the system, which contain N identical spherical particles. n-particle distribution function is defined by:

$$\rho^{(n)}(\mathbf{r^N}) = \frac{N!}{(N-n)!} \int \frac{1}{Q_N} e^{-\beta(U_N + U_{N,ext})} d\mathbf{r_{n+1}} \dots d\mathbf{r_N} \tag{1}$$

We separate a potential energy into the two terms: interaction of the first particle with others and interaction between otner $N-1$ partivles:

$$U_N(\mathbf{r^N}) = \sum_{i=2}^{N} u(|\mathbf{r_1} - \mathbf{r_i}|) + \sum_{i=2}^{N} \sum_{2<j<i} u(|\mathbf{r_i} - \mathbf{r_j}|) \tag{2}$$

And the same for the extenal energy:

$$U_{N,ext}(\mathbf{r^N}) = u_{ext}(\mathbf{r_1}) + \sum_{i=2}^{N} u_{ext}(\mathbf{r_i}) \tag{3}$$

Taking a partial derivative of (1) with respect to $\mathbf{r_1}$ we have:

$$\frac{\partial}{\partial \mathbf{r_1}} \rho^{(n)}(\mathbf{r_1}, \dots, \mathbf{r_n}) = -\beta \frac{N!}{(N-n)!} \int \frac{1}{Q_N} e^{-\beta(U_N + U_{N,ext})} \left(\sum_{i=2}^{N} \frac{\partial u(|\mathbf{r_1} - \mathbf{r_i}|)}{\partial \mathbf{r_1}} + \frac{\partial u_{ext}(\mathbf{r_1})}{\partial \mathbf{r_1}} \right) d\mathbf{r_{n+1}} \dots d\mathbf{r_N}$$

$$= -\beta \frac{N!}{(N-n)!} \int \frac{1}{Q_N} e^{-\beta(U_N + U_{N,ext})} \sum_{i=2}^{N} \frac{\partial u(|\mathbf{r_1} - \mathbf{r_i}|)}{\partial \mathbf{r_1}} d\mathbf{r_{n+1}} \dots d\mathbf{r_N} - \beta \frac{N!}{(N-n)!} \frac{\partial u_{ext}(\mathbf{r_1})}{\partial \mathbf{r_1}} \int \frac{1}{Q_N} e^{-\beta(U_N + U_{N,ext})} d\mathbf{r_n}$$

$$= -\beta \frac{N!}{(N-n)!} \int \frac{1}{Q_N} e^{-\beta(U_N + U_{N,ext})} \sum_{i=2}^{N} \frac{\partial u(|\mathbf{r_1} - \mathbf{r_i}|)}{\partial \mathbf{r_1}} d\mathbf{r_{n+1}} \dots d\mathbf{r_N} - \beta \frac{\partial u_{ext}(\mathbf{r_1})}{\partial \mathbf{r_1}} \rho^{(n)}(\mathbf{r_1}, \dots, \mathbf{r_n}) \tag{4}$$

Now, if we rewrite

$$\sum_{i=2}^{N} \frac{\partial u(|\mathbf{r_1} - \mathbf{r_i}|)}{\partial \mathbf{r_1}} = \sum_{i=2}^{n} \frac{\partial u(|\mathbf{r_1} - \mathbf{r_i}|)}{\partial \mathbf{r_1}} + \sum_{i=n+1}^{N} \frac{\partial u(|\mathbf{r_1} - \mathbf{r_i}|)}{\partial \mathbf{r_1}} \tag{5}$$

We have

$$\frac{\partial}{\partial \mathbf{r_1}} \rho^{(n)}(\mathbf{r_1}, \dots, \mathbf{r_n}) = -\beta \frac{N!}{(N-n)!} \sum_{i=2}^{n} \frac{\partial u(|\mathbf{r_1} - \mathbf{r_i}|)}{\partial \mathbf{r_1}} \int \frac{1}{Q_N} e^{-\beta(U_N + U_{N,ext})} d\mathbf{r_{n+1}} \dots d\mathbf{r_N}$$

$$-\beta \frac{N!}{(N-n)!} \sum_{i=n+1}^{N} \int \frac{\partial u(|\mathbf{r_1}-\mathbf{r_i}|)}{\partial \mathbf{r_1}} \frac{1}{Q_N} e^{-\beta(U_N+U_{N,ext})} d\mathbf{r_{n+1}} \dots d\mathbf{r_N} - \beta \frac{\partial u_{ext}(\mathbf{r_1})}{\partial \mathbf{r_1}} \rho^{(n)}(\mathbf{r_1}, \dots, \mathbf{r_n}) \tag{6}$$

The energy U_N is symmetric with respect to the coordinate permutations. That's why

$$\int \frac{\partial u(|\mathbf{r_1}-\mathbf{r_i}|)}{\partial \mathbf{r_1}} \frac{1}{Q_N} e^{-\beta(U_N+U_{N,ext})} d\mathbf{r_{n+1}} \dots d\mathbf{r_N} = \int \frac{\partial u(|\mathbf{r_1}-\mathbf{r_{n+1}}|)}{\partial \mathbf{r_1}} \frac{1}{Q_N} e^{-\beta(U_N+U_{N,ext})} d\mathbf{r_{n+1}} \dots d\mathbf{r_N} \tag{7}$$

Putting it to (6) we have:

$$\frac{\partial}{\partial \mathbf{r_1}} \rho^{(n)}(\mathbf{r_1}, \dots, \mathbf{r_n}) = -\beta \frac{N!}{(N-n)!} \sum_{i=2}^{n} \frac{\partial u(|\mathbf{r_1}-\mathbf{r_i}|)}{\partial \mathbf{r_1}} \rho^{(n)}$$

$$-\beta \frac{(N-n)\cdot N!}{(N-n)!} \int \frac{\partial u(|\mathbf{r_1}-\mathbf{r_{n+1}}|)}{\partial \mathbf{r_1}} \frac{1}{Q_N} e^{-\beta(U_N+U_{N,ext})} d\mathbf{r_{n+1}} \dots d\mathbf{r_N} - \beta \frac{\partial u_{ext}(\mathbf{r_1})}{\partial \mathbf{r_1}} \rho^{(n)}(\mathbf{r_1}, \dots, \mathbf{r_n}) \tag{8}$$

We can see, that

$$-\beta \frac{(N-n)\cdot N!}{(N-n)!} \int \frac{\partial u(|\mathbf{r_1}-\mathbf{r_{n+1}}|)}{\partial \mathbf{r_1}} \frac{1}{Q_N} e^{-\beta(U_N+U_{N,ext})} d\mathbf{r_{n+1}} \dots d\mathbf{r_N}$$

$$= -\beta \int \frac{\partial u(|\mathbf{r_1}-\mathbf{r_{n+1}}|)}{\partial \mathbf{r_1}} \left(\frac{N!}{(N-(n+1))!} \int \frac{1}{Q_N} e^{-\beta(U_N+U_{N,ext})} d\mathbf{r_{n+2}} \dots d\mathbf{r_N} \right) d\mathbf{r_{n+1}}$$

$$= -\beta \int \frac{\partial u(|\mathbf{r_1}-\mathbf{r_{n+1}}|)}{\partial \mathbf{r_1}} \rho^{(n+1)}(\mathbf{r_1}, \dots, \mathbf{r_{n+1}}) d\mathbf{r_{n+1}}$$

When we have relation between the n-particle and (n+1)-particle distributions:

$$\frac{\partial}{\partial \mathbf{r_1}} \rho^{(n)}(\mathbf{r_1}, \dots, \mathbf{r_n}) = -\beta \frac{N!}{(N-n)!} \sum_{i=2}^{n} \frac{\partial u(|\mathbf{r_1}-\mathbf{r_i}|)}{\partial \mathbf{r_1}} \rho^{(n)}$$

$$-\beta \int \frac{\partial u(|\mathbf{r_1}-\mathbf{r_{n+1}}|)}{\partial \mathbf{r_1}} \rho^{(n+1)}(\mathbf{r_1}, \dots, \mathbf{r_{n+1}}) d\mathbf{r_{n+1}} - \beta \frac{\partial u_{ext}(\mathbf{r_1})}{\partial \mathbf{r_1}} \rho^{(n)}(\mathbf{r_1}, \dots, \mathbf{r_n}) \tag{9}$$

Multiplying both parts by $(-k_B T)$ we have the formula:

$$-k_B T \frac{\partial}{\partial \mathbf{r_1}} \rho^{(n)} = \rho^{(n)} \frac{\partial}{\partial \mathbf{r_1}} u_{ext}(\mathbf{r_1}) + \rho^{(n)} \sum_{2}^{n} \frac{\partial}{\partial \mathbf{r_1}} u(|\mathbf{r_1}-\mathbf{r_i}|) + \int \frac{\partial u(|\mathbf{r_1}-\mathbf{r_{n+1}}|)}{\partial \mathbf{r_1}} \rho^{(n+1)} d\mathbf{r_{n+1}} \tag{10}$$

The most interesting cases are $n = 1$:

$$-k_B T \frac{\partial}{\partial \mathbf{r_1}} \rho^{(1)} = \rho^{(1)} \frac{\partial}{\partial \mathbf{r_1}} u_{ext}(\mathbf{r_1}) + \int \frac{\partial u(|\mathbf{r_1}-\mathbf{r_2}|)}{\partial \mathbf{r_1}} \rho^{(2)} d\mathbf{r_2} \tag{11}$$

and $n = 2$:

$$-k_B T \frac{\partial}{\partial \mathbf{r_1}} \rho^{(2)} = +\rho^{(2)} \frac{\partial}{\partial \mathbf{r_1}} u(|\mathbf{r_1}-\mathbf{r_2}|) \rho^{(2)} \frac{\partial}{\partial \mathbf{r_1}} u_{ext}(\mathbf{r_1}) + \int \frac{\partial u(|\mathbf{r_1}-\mathbf{r_3}|)}{\partial \mathbf{r_1}} \rho^{(3)} d\mathbf{r_3} \tag{12}$$

In the case (11) for the non-interacting particles the relation 10 becomes a barometric formula:

$$-k_B T \frac{\partial}{\partial \mathbf{r_1}} \rho^{(1)} = \rho^{()} \frac{\partial}{\partial \mathbf{r_1}} u_{ext}(\mathbf{r_1}) \tag{13}$$

Dividing both parts by ρ:

$$-k_B T \frac{\partial \rho^{(1)}}{\partial \mathbf{r_1}} \cdot \frac{1}{\rho^{(1)}} = \frac{\partial}{\partial \mathbf{r_1}} u_{ext}(\mathbf{r_1}) \tag{14}$$

And using the rule for finding logarithm derivative we have:

$$\frac{\partial \ln \rho^{(1)}}{\partial \mathbf{r_1}} = \frac{\partial}{\partial \mathbf{r_1}} \left(-\beta u_{ext}(\mathbf{r_1})\right) \tag{15}$$

In the case $n = 2$ we may use an approximation

$$\rho^(3)(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_3}) = \frac{\rho^(2)(\mathbf{r_1}, \mathbf{r_2})\rho^(2)(\mathbf{r_1}, \mathbf{r_3})\rho^(2)(\mathbf{r_2}, \mathbf{r_3})}{\rho^(1)(\mathbf{r_1})\rho^(1)(\mathbf{r_2})\rho^(1)(\mathbf{r_3})} \tag{16}$$

This leads to the equation

$$-kT \frac{\partial}{\partial \mathbf{r_1}} \rho(12) = \rho(12) \frac{\partial}{\partial \mathbf{r_1}} u(12) + \rho(12) \frac{\partial}{\partial \mathbf{r_1}} u_{ext} + \int \frac{\partial u(13)}{\partial \mathbf{r_1}} \frac{\rho(12)\rho(13)\rho(23)}{\rho(1)\rho(2)\rho(3)} d3 \tag{17}$$

we consider the uniform case:

$$\rho(12) = \rho^2 g(12) \tag{18}$$

and dividing both parts by $\rho(12)$ we have

$$-kT \frac{\partial g(12)}{\partial \mathbf{r_1} g(12)} = \frac{\partial}{\partial \mathbf{r_1}} u(12) + \frac{\partial}{\partial \mathbf{r_1}} u_{ext} + \rho \int \frac{\partial u(13)}{\partial \mathbf{r_1}} g(13) g(23) d3 \tag{19}$$

using the formula for differential of logarithm we have:

$$-kT \frac{\partial \ln g(12)}{\partial \mathbf{r_1}} = \frac{\partial}{\partial \mathbf{r_1}} u(12) + \frac{\partial}{\partial \mathbf{r_1}} u_{ext} + \rho \int \frac{\partial u(13)}{\partial \mathbf{r_1}} g(13) g(23) d3 \tag{20}$$

when $\rho- > 0$ we have:

$$\rho(12) = exp(-\beta u(12)) \tag{21}$$